cumene (Stream 9) is recycled. The uncondensed vapors from the condenser are vented (Vent C).

The concentrated CHP (Stream 10) is transferred through a surge tank to the cleavage reactor (Stream 11). Sulfuric acid, diluted to 5 to 10 percent with acetone (Stream 12), is added to catalyze the decomposition of CHP to acetone and phenol. Uncondensed vapors captured from the cleavage reactor are vented (Vent D). Excess acid in the cleaved mixture (Stream 13) is neutralized with sodium hydroxide solution (Stream 14). The neutralized product (Stream 15) flows through the crude-product surge tank to a multi-column distillation train to produce product-grade acetone, phenol, and AMS. 80

The crude product is separated in the first distillation column into a crude acetone fraction (Stream 16) and a crude phenol stream (Stream 17). The crude acetone (Stream 16) is combined with recycled hydrocarbons from the phenol topping column (Stream 18) and fed through a surge tank to the light-ends column (Stream 19) to strip low-boiling hydrocarbon impurities, such as acetaldehyde and formaldehyde, which are vented to the atmosphere (Vent E).

The bottoms stream from the light-ends column (Stream 20) is fed to the acetone finishing column, where the acetone is distilled overhead, condensed (Stream 21), and sent to day tanks and subsequently to acetone product storage and loading. Uncondensed vapors are vented (Vent F). The bottoms stream (Stream 22) is processed to produce AMS (not shown).⁸⁰

The crude phenol stream (Stream 17) and the bottoms from the phenol finishing column (Stream 23) are fed to the heavy-ends column and distilled under vacuum to separate tars (Stream 24) from the impure phenol stream (Stream 25).⁸⁰ Uncondensed vapors from the condenser following the heavy-ends column are vented (Vent G).

The impure phenol is fed to the phenol topping column to remove hydrocarbons such as cumene and AMS. The overhead stream from the phenol topping column (Stream 18)

may be condensed and recycled to the light-ends column of the acetone process for removal of residual acetone, cumene, and AMS. The uncondensed vapors from the condenser following the phenol topping column are vented (Vent H). The phenolic stream (Stream 26) is then fed to a dehydrating column, where water is removed overhead as a phenol/water azeotrope. Uncondensed vapors are vented (Vent I).⁸⁰

The dried phenol stream (Stream 27) is distilled under vacuum in the phenol finishing column to separate product-quality phenol (Stream 28) from higher boiling components (Stream 23), which are recycled to the heavy ends column. Uncondensed vapors from the condenser after the phenol finishing column are vented (Vent J). The product-quality phenol is stored in tanks for subsequent loading.⁸⁰

Toluene Oxidation Process

In this process, toluene is oxidized by air to benzoic acid. Following separation, the benzoic acid is catalytically converted to phenol.

5.4.2 Benzene Emissions from Phenol Production

Information related to benzene emissions from process vents, equipment leaks, storage vessels, wastewater collection and treatment systems, and product loading and transport operations associated with phenol production is presented below. Where a literature review revealed no source-specific emission factors for uncontrolled or controlled benzene emissions from these emission points, the reader is referred to Section 5.10 of this chapter, which provides a general discussion of methods for estimating uncontrolled and controlled benzene emissions from these types of emission points.

"Spent air" from the oxidizer reactor (Vent A, Figure 5-9) is the largest source of benzene emissions at phenol production plants utilizing the Allied process.⁸⁷ Table 5-7 provides uncontrolled and controlled (i.e., thermal oxidizer) emission factors from the oxidizer

TABLE 5-7. SUMMARY OF EMISSION FACTORS FOR PHENOL PRODUCTION BY THE PEROXIDATION OF CUMENE

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg) ^a	Factor Rating	Reference
3-01-202-02 Phenol Manufacturing - Cumene Oxidation	Process Vent	Uncontrolled ^b	4.00×10^{-3} (2.00 x 10^{-3})	U	3
3-01-202-02 Phenol Manufacturing - Cumene Oxidation	Process Vent	Thermal Oxidizer	$1.16 \times 10^{-4} $ (5.82 x 10^{-5})	D	88, 89

^a Factors are expressed in lb (kg) benzene emitted for ton (Mg) cumene produced. ^b Measured at post oxidizer condenser vent.

reactor vent from the phenol production process based on the peroxidation of cumene.^{88,89} Charcoal adsorption is the most commonly used method to control emissions from the oxidizer reactor vent; however, condensation, absorption, and thermal oxidation have also been used.⁹⁰ Recovery devices (i.e., one or more condensers and/or absorbers) are the most commonly used methods to recover product and control emissions from the cleavage (Vent D, Figure 5-9) and product purification distillation columns; however, adsorption and incineration have also been used for emissions reduction.^{81,90}

5.5 NITROBENZENE PRODUCTION

Benzene is a major feedstock in commercial processes used to produce nitrobenzene. Approximately 5 percent of benzene production in the United States is used in the production of nitrobenzene.¹² In these processes, benzene is directly nitrated with a mixture of nitric acid, sulfuric acid, and water.

As of February 1991, five companies were producing nitrobenzene in the United States.⁹¹ Their names and plant locations are shown in Table 5-8.¹¹ In addition to these plants, plans are underway for Miles and First Chemical to start up a possible 250-million-pound (113.4-Gg) aniline plant, along with feedstock nitrobenzene, at Baytown, Texas.⁹²

A discussion of the nitrobenzene production process, potential sources of benzene emissions, and control techniques is presented in this section. Unless otherwise referenced, the information that follows has been taken directly from Reference 93.

5.5.1 Process Descriptions for Continuous Nitration

Nitrobenzene is produced by a highly exothermic reaction in which benzene is reacted with nitric acid in the presence of sulfuric acid. Most commercial plants use a continuous

TABLE 5-8. PRODUCERS OF NITROBENZENE

Company	Location	Capacity in million lb/yr (million kg/yr)
Rubicon, Inc.	Geismar, LA	550 (250)
First Chemical Corporation	Pascagoula, MS	536 (244)
E.I. duPont de Nemours and Company, Inc.	Beaumont, TX	350 (160)
BASF Corporation (Polymers Division Urethanes)	Geisman, LA	250 (110)
Miles, Inc. (Polymers Division Polyurethane)	New Martinsville, WV	100 (45)
TOTAL		1,786 (809)

Source: Reference 11.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc.

The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

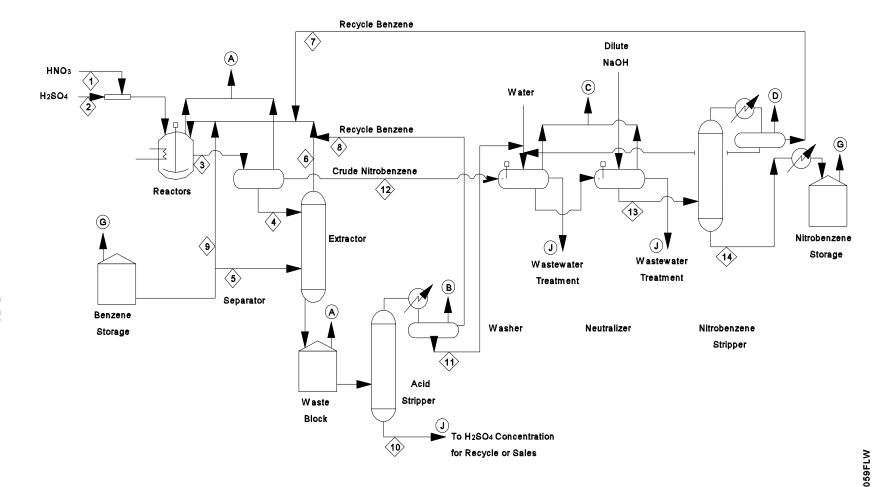
These data on producers and location were current as of January 1993.

nitration process, where benzene and the acids are mixed in a series of continuous stirred-tank reactors. A flow diagram of the basic continuous process is shown in Figure 5-11.

93

As shown in the figure, nitric acid (Stream 1) and sulfuric acid (Stream 2) are mixed before flowing into the reactor. Benzene extract (Stream 6), two recovered and recycled benzene streams (Streams 7 and 8), and as much additional benzene (Stream 9) as is required are combined to make up the benzene charge to the reactor.

For the process depicted here, nitration occurs at 131°F (55°C) under atmospheric pressure. Cooling coils are used to remove the heat generated by the reaction.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-11. Process Flow Diagram for Manufacture of Nitrobenzene

Following nitration, the crude reaction mixture (Stream 3) flows to the decanter, where the organic phase of crude nitrobenzene is separated from the aqueous waste acid. The crude nitrobenzene (Stream 12) subsequently flows to the washer and neutralizer, where mineral (inorganic) and organic acids are removed. The washer and neutralizer effluent are discharged to wastewater treatment. The organic layer (Stream 13) is fed to the nitrobenzene stripper, where water and most of the benzene and other low-boiling-point components are carried overhead. The organic phase carried overhead is primarily benzene and is recycled (Stream 7) to the reactor. The aqueous phase (carried overhead) is sent to the washer. Stripped nitrobenzene (Stream 14) is cooled and then transferred to nitrobenzene storage.

The treatment, recycling, or discharge of process streams is also shown in the flow diagram. Aqueous waste acid (Stream 4) from the decanter flows to the extractor, where it is denitrated. There, the acid is treated with fresh benzene from storage (Stream 5) to extract most of the dissolved nitrobenzene and nitric acid. The benzene extract (Stream 6) flows back to the nitrating reactor, whereas the denitrated acid is stored in the waste acid tank.

Benzene is commonly recovered from the waste acid by distillation in the acid stripper. The benzene recovered is recycled (Stream 8), and water carried overhead with the benzene is forwarded (Stream 11) to the washer. The stripped acid (Stream 10) is usually reconcentrated on site but may be sold.⁹³

Typically, many of the process steps are padded with nitrogen gas to reduce the chances of fire or explosion. This nitrogen padding gas and other inert gases are purged from vents associated with the reactor and separator (Vent A in Figure 5-11), the condenser on the acid stripper (Vent B), the washer and neutralizer (Vent C), and the condenser on the nitrobenzene stripper (Vent D).

5.5.2 Benzene Emissions from Nitrobenzene Production

Benzene emissions may occur at numerous points during the manufacture of nitrobenzene. These emissions may be divided into four types: process emissions, storage emissions, equipment leak emissions, and secondary emissions.

Process emissions occur at the following four gas-purge vents: the reactor and separator vent (A), the acid stripper vent (B), the washer and neutralizer vent (C), and the nitrobenzene stripper vent (D). The bulk of benzene emissions occur from the reactor and separator vent. This vent releases about three times the level of benzene released from Vents B and D (Figure 5-11), and about 120 times that released from Vent C. For all of these vents, the majority of VOC emissions is in the form of benzene. Benzene accounts for 99, 100, 76, and 99 percent of total VOC emissions from Vents A, B, C, and D, respectively. Table 5-9 shows estimated emission factors for benzene from these sources. 93

Other emissions include storage, equipment leak, and secondary emissions. Storage emissions (G) occur from tanks storing benzene, waste acid, and nitrobenzene. Equipment leak emissions of benzene can occur when leaks develop in valves, pump seals, and other equipment. Leaks can also occur from corrosion by the sulfuric and nitric acids and can hinder control of fugitive emissions.

Secondary emissions can result from the handling and disposal of process waste liquid. Three potential sources of secondary benzene emissions (J) are the wastewater from the nitrobenzene washer, waste caustic from the nitrobenzene neutralizer, and waste acid from the acid stripper. Where waste acid is not stripped before its sale or reconcentration, secondary emissions will be significantly affected (increased) unless the reconcentration process is adequately controlled.

Table 5-9 gives benzene emission factors before and after the application of possible controls for two hypothetical plants using the continuous nitration process. The two

TABLE 5-9. SUMMARY OF EMISSION FACTORS FOR HYPOTHETICAL NITROBENZENE PRODUCTION PLANTS

SCC and Description	Emissions Source ^a	Control Device	Emission Factor in lb/ton (g/kg) ^b	Factor Rating
3-01-195-01	Small Benzene Storage ^c (Point G)	Uncontrolled	$0.156 (0.078)^{d}$	U
Nitrobenzene - General			$0.154 (0.077)^{e}$	U
3-01-195-01	Benzene Storage ^c	Uncontrolled	$0.566 (0.283)^{d}$	U
Nitrobenzene - General	(Point G)		0.562 (0.281) ^e	U
		Internal Floating Roof	0.085 (0.0425) ^{d,e}	U
3-01-195-01 Nitrobenzene - General	Secondary (Point J)	Uncontrolled	0.20 (0.10) ^{d,e}	U
3-01-195-01 Nitrobenzene - General	Total	Uncontrolled	4.9 (2.45) ^d	U
			4.4 (2.19) ^e	U
		Vent Adsorber	$0.78 (0.39)^{d}$	U
			0.64 (0.32) ^e	U
		Thermal Oxidizer	$0.44~(0.22)^{d}$	U
			0.52 (0.26) ^e	U
3-01-195-03 Nitrobenzene - Acid Stripper Vent	Waste-Acid Stripper (Point B)	Uncontrolled	0.034 (0.170) ^{d,e}	U
3-01-195-04	Wash and Neutralization	Uncontrolled	0.0162 (0.0081) ^{d,e}	U
Nitrobenzene - Washer/Neutralizer Vent	(Point C)	Vent Adsorber	0.155 (0.0776) ^{d,e}	U (continued)

(continued)

TABLE 5-9. CONTINUED

SCC and Description	Emissions Source ^a	Control Device	Emission Factor in lb/ton (g/kg) ^b	Factor Rating
3-01-195-05	Nitrobenzene Stripper	Uncontrolled	$0.34 (0.170)^{d,e}$	U
Nitrobenzene - Nitrobenzene Stripper Vent	(Point D)	Thermal Oxidizer	0.0288 (0.0144) ^{d,e}	U
3-01-195-06	Waste Acid Storage	Uncontrolled	0.102 (0.051) ^{d,e}	U
Nitrobenzene - Waste Acid Storage	(Point G)		0.96 (0.048) ^{d,e}	U
3-01-195-80 Nitrobenzene - Equipment Leak Emissions	Process Pumps and Valves ^f	Uncontrolled	$1.26 (0.63)^{d}$	U
			0.76 (0.38) ^e	U
		LD&R plus mechanical seals	$0.33 (0.165)^{d}$	U
			0.198 (0.099) ^e	U

Source: Reference 93.

For 198 million lb/yr (90,000 Mg/yr) Model Plant

	Tank Size ft ³ (m ³)	Turnovers/Year	Bulk Liquid Temperature °F (°C)	
Benzene (large tank)	100,292 (2,840)	24	68 (20)	
Benzene (small tank)	10,029 (284)	236	68 (20)	
	For 331 million lb/yr (150,000 Mg/yr) Model Plant			
	Tank Size ft ³ (m ³)	Turnovers/Year	Bulk Liquid Temperature °F (°C)	
Benzene (large tank)	160,035 (4,730)	24	68 (20)	
Benzene (small tank)	16,704 (473)	236	68 (20)	

(continued)

Emission points refer to Figure 5-11.
 Factors are expressed as lb (g) benzene emitted per ton (kg) nitrobenzene produced.
 Storage emission factors are based on these tank parameters:

TABLE 5-9. CONTINUED

- ^d Emission factor for a hypothetical 198 million lb/yr (90,000 Mg/yr) capacity plant.
- ^e Emission factor for a hypothetical 331 million lb/yr (150,000 Mg/yr) capacity plant.
- Process pumps and valves are potential sources of fugitive emissions. Each model plant is estimated to have 42 pumps (including 17 spares), 500 process valves, and 20 pressure-relief valves based on data from an existing facility. All pumps have mechanical seals. Twenty-five percent of these pumps and valves are being used in benzene service. The fugitive emissions included in this table are based on the factors given in Section 4.5.2.

plants differ in capacity; one produces 198 million lb/yr (90,000 Mg/yr) and the other 331 million lb/yr (150,000 Mg/yr) of nitrobenzene. Both plants use a vent absorber or thermal oxidizer to control process emissions in conjunction with waste-acid storage and small benzene storage emissions.

The values presented for the main benzene storage emissions were calculated by assuming that a contact-type internal floating roof with secondary seals will reduce fixed-roof tank emissions by 85 percent. The values presented for controlled equipment leak emissions are based on the assumption that leaks from valves and pumps, resulting in concentrations greater than 10,000 ppm on a volume basis, are detected, and that appropriate measures are taken to correct the leaks.

Secondary emissions and nitrobenzene storage emissions are assumed to be uncontrolled. Uncontrolled emission factors are based on the assumptions given in the footnotes to Table 5-9. The total controlled emission factors for these hypothetical plants range from 0.44 to 0.78 lb/ton (0.22 to 0.39 kg/Mg). Actual emissions from nitrobenzene plants would be expected to vary, depending on process variations, operating conditions, and control methods.⁹³

A variety of control devices may be used to reduce emissions during nitrobenzene production, but insufficient information is available to determine which devices nitrobenzene producers are using currently. Process emissions may be reduced by vent absorbers, water scrubbers, condensers, incinerators, and/or thermal oxidizers.

Storage emissions from the waste-acid storage tank and the small benzene storage tank can be readily controlled in conjunction with the process emissions. (A small storage tank contains approximately one day's supply of benzene; the larger tank is the main benzene storage tank.) In contrast, emissions from the main benzene storage tanks are controlled by using floating-roof storage tanks.

Equipment leak emissions are generally controlled by leak detection and repair, whereas secondary emissions are generally uncontrolled.

5.6 ANILINE PRODUCTION

Almost 97 percent of the nitrobenzene produced in the United States is converted to aniline.⁹¹ Because of its presence as an impurity in nitrobenzene, benzene may be emitted during aniline production. Therefore, a brief discussion of the production of aniline from nitrobenzene and its associated benzene emissions is included in this document.

Table 5-10 lists the U.S. producers of aniline and the production method.¹¹ The main derivative of aniline (75 percent) is p.p.-methylene diphenyl diisocyanate (MDI). The growth outlook for aniline is expected to remain strong because of its continued use in housing and automobile parts.⁹⁵

5.6.1 <u>Process Descriptions for Aniline Production for Nitrobenzene</u>

A process flow diagram of the most widely used process for manufacturing of aniline--by hydrogen reduction of nitrobenzene--is shown in Figure 5-12. As shown in the figure, nitrobenzene (Stream 1) is vaporized and fed with excess hydrogen (Stream 2) to a fluidized-bed reactor. The product gases (Stream 3) are passed through a condenser. The condensed materials are decanted (Stream 4), and non-condensible materials are recycled to the reactor (Stream 5). In the decanter, one phase (Stream 6) is crude aniline and the other is an aqueous phase (Stream 7).

The crude aniline phase is routed to a dehydration column that operates under vacuum. Aniline is recovered from the aqueous phase by stripping or extraction with nitrobenzene. Overheads from the dehydration column (Stream 8) are condensed and recycled to the decanter. The bottoms from the dehydration column (Stream 9), which contain aniline,

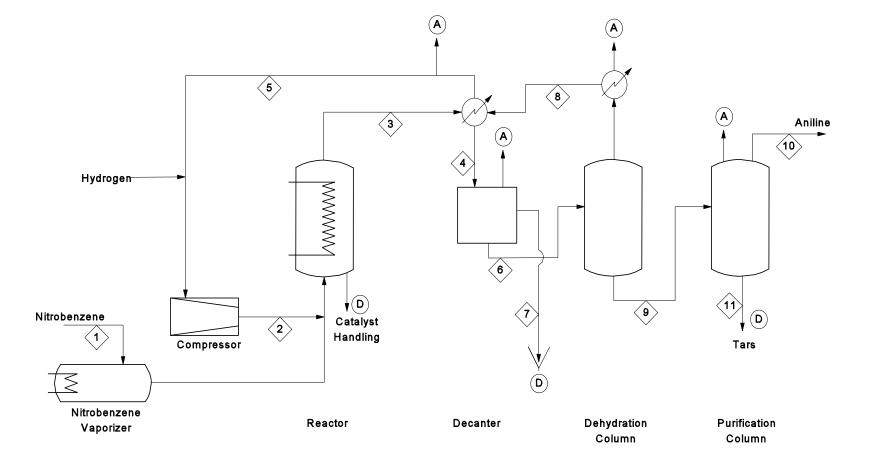
TABLE 5-10. U.S. PRODUCERS OF ANILINE

Facility	Location	Annual Capacity in million gal/yr (million kg/yr)	Process and Remarks
Aristech Chemical Corporation	Haverhill, OH	200 (90)	Ammonolysis of phenol (Halcon process)
E.I. duPont de Nemours and Company, Inc.			
duPont Chemicals	Beaumont, TX	260 (120)	Hydrogen reduction of nitrobenzene
First Chemical Corporation	Pascagoula, MS	275 (130)	Hydrogen reduction of nitrobenzene
ICI American Holdings, Inc. and Uniroyal, Inc. Affiliate			
Rubicon, Inc.	Geismar, LA	400 (180)	Hydrogen reduction of nitrobenzene
Miles, Inc.			
Polymers Polyurethane Division	New Martinsville, WV	40 (20)	Nitrobenzene (acid-iron reduction process)
BASF Corporation Polymers Division Urethanes	Geismar, LA	190 (90)	
TOTAL		1,365 (630)	

Source: Reference 11.

Note:

This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These data on producers and locations were current as of January 1, 1993.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-12. Flow Diagram for Manufacture of Aniline

Source: Reference 96.

are sent to the purification column. Overheads (Stream 10) from the purification column contain the aniline product, while the bottoms (Stream 11) contain tars.

Fourteen percent of current aniline production (produced by Miles, Inc.) involves an acid-iron reduction process where iron oxide is created as a co-product. Nitrobenzene is reacted with iron and dilute hydrochloric acid at reflux. When the reaction is complete, the aniline-water mixture is separated from the iron-hydroxide sludge and the heavier aniline layer is removed and vacuum distilled to yield purified aniline.¹⁸

5.6.2 <u>Benzene Emissions from Aniline Production</u>

Process emissions of benzene typically originate from the purging of noncondensibles during recycle to the reactor and purging of inert gases from separation and purification equipment (Vent A in Figure 5-12).⁹

Only one emission factor was found for benzene emissions from aniline production. For process vents (Vent A), an uncontrolled emission factor of 0.0114 lb benzene/ton aniline produced (0.0057 kg/Mg) was reported in the literature. ⁹⁶ The SCC code for this emission point is 3-01-034-03: Aniline-Reactor Recycle Process Vent. No details of the emission factor derivation were provided, other than it was based on data provided by an aniline producer, so it was assigned a U rating.

Control techniques available for emissions associated with the purging of equipment vents include water scrubbing and thermal oxidation. No data were found to indicate the efficiencies of these control devices for benzene emissions. The reader is urged to contact specific production facilities before applying the emission factor given in this report to determine exact process conditions and control techniques.

5.7 CHLOROBENZENE PRODUCTION

The most important chlorobenzenes for industrial applications are monochlorobenzene (MCB), dichlorobenzene (DCB), and trichlorobenzene (TCB). Therefore, this section focuses on benzene emissions associated with production of these three types of chlorobenzenes. Table 5-11 lists the U.S. producers of MCB, DCB, and TCB. The producing companies' capabilities are flexible, such that different chlorobenzenes may be isolated, depending on market demand. DCBs and TCBs are produced in connection with MCB. The relative amounts of the products can be varied by process control.⁹⁷

5.7.1 <u>Process Description for Chlorobenzene Production by Direct Chlorination of</u> Benzene

The most widely used process for the manufacture of chlorobenzenes is direct chlorination of benzene in the presence of ferric chloride catalyst to produce MCB and DCB. HCl is a by-product. The two major isomers of DCB are ortho and para. As chlorination continues, tri-, tetra-, penta-, and, finally, hexachlorobenzenes are formed. However, TCB is the only one of the more highly chlorinated products found in significant amounts.

Basic operations that may be used in the continuous production of MCB are shown in Figure 5-13. ¹⁹ The process begins with a series of small, externally cooled cast iron or steel vessels containing the catalyst (which may consist of Rashing rings of iron or iron wire). Chlorine is supplied into each vessel through suitably positioned inlets to maintain a large benzene-to-chlorine reaction at all points along the reaction stream. The temperature is held between 68 to 104°F (20 to 40°C) to minimize the production of DCBs, which form at higher temperatures. Dry benzene (Stream 1) and dried recycled benzene (Stream 2) are introduced into the reactor, which produces an overhead gas (Stream 3).

The gas stream (containing HCl, unreacted chlorine, inert gases from the chlorine feed, benzene, and other VOC) is sent to an organic absorber, where benzene and

TABLE 5-11. U.S. PRODUCERS OF MONO-, DI-, AND TRICHLOROBENZENE

Company	Location	Product	Annual Capacity million lb (million kg)
Monsanto Company Chemical Group	Sauget, IL	Monochlorobenzene o-Dichlorobenzene p-Dichlorobenzene	176 (80) 11 (5) 22 (10)
PPG Industries, Inc. Chemical Group	Natrium, WV	Monochlorobenzene o-Dichlorobenzene p-Dichlorobenzene	45 (20) 20 (9) 30 (14)
Standar Chlorine Chemical Company, Inc.	Delaware City, DE	Monochlorobenzene o-Dichlorobenzene p-Dichlorobenzene 1,2,3-Trichlorobenzene 1,2,4-Trichlorobenzene	150 (68) 50 (23) 75 (34) NA NA
Southland Corporation Chemical Division	Great Meadows, NJ	1,3,5-Trichlorobenzene	NA

Source: Reference 11.

NA = Not available

Note:

This is a list of major facilities producing mono-, di-, and trichlorobenzene. The list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current lists or the plants themselves. The level of emissions from any given facility is a function of variables such as throughput and control measures, and should be determined through direct contacts with plant personnel. The data on producers and locations were current as of January 1993.